

Crystallization Behavior of PET Materials

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Abstract

Polyethylene terephthalate, commonly coded as PET, PETE, is a thermoplastic polymer resin of the polyesters and is used in liquid containers, drinks, food and synthetic fibres. Depending on its processing and thermal conditions, PET may exist both as amorphous and as semi-crystalline. PET may appear opaque, white and transparent depending on its crystalline and amorphous structure. Its crystallinity and consequently its physical and mechanical properties are highly dependent on processing conditions like processing temperature, cooling rate, stretching process etc. In this study, it was tried to summarize all about PET crystallization by referring to all studies carried out before. Crystallization is very significant properties affecting all mechanical and physical properties of PET just as for all kind of polymers. As a result, this subject has taken in very good interest so far and it is believed that this interest will go on increasingly.

Keywords: Crystallization, material properties, PET

PET Malzemelerin Kristalizasyon Davranışı

Özet

Polyethylene terephthalate, PET veya PETE şeklinde kısaltması yapılan, sıvıların, yiyecek ve içeceklerin saklanması ve taşınmasında, sentetik liflerin yapımında kullanılan polyester sınıfından termoplastik polimer bir reçinedir. Termal ve proses şartlarına bağlı olarak, PET amorf ya da semi-kristal yapıda olabilir. Bu özelliğinden dolayı PET donuk, beyaz ya da camsı bir yapıda olabilir. PET'in kristal yapısı, buna bağlı olarak da fiziksel ve mekaniksel özellikleri büyük oranda işlem sıcaklığı, soğutma hızı, gerdirme işlemi gibi proses parametrelerine bağlıdır. Bu çalışmada, PET'nin kristalizasyonu ile ilgili daha önce yapılan bütün çalışmalar özetlenmeye çalışılmıştır. Tıpkı bütün polimerlerde olduğu gibi kristalizasyon PET'nin bütün fiziksel ve

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mekaniksel özelliklerini etkileyen çok önemli bir özelliktir. Sonuç olarak, bu konu şimdiye kadar bir hayli ilgi çekmiştir ve bu ilginin daha da artacağına inanılmaktadır.

Anahtar kelimeler: Kristalizasyon, malzeme özellikleri, PET

1. Introduction

PET has the most application among plastics and is found most commonly in daily life. It is used especially in containers produced for storing and carrying food and liquids; in particular carbonated soft drinks (CSDs). However, some cracking problems have been observed at the bottom of bottles; due to either the geometrical shape of the petaloid base or the process parameters.

In this literature review the development of the PET bottle was reviewed, followed by a discussion of physical and chemical properties of PET and the factors that affect these properties. Then the problem of cracks occurring in the bottle base will be reviewed and its causes investigated in our following review paper.

2. Development of the PET bottle

PET poly (ethylene terephthalate) was developed in the 1940's and since then it has played an important role in the food and beverage packaging industry [1]. Due to its popularity the use of PET in carbonated soft drinks bottles has been studied extensively [2]. Initially, PET bottles consisted of two pieces; the blown bottle section, and a separate 'cap' section fitted over the over the hemispherical bottle base. The polyethylene cap section made the bottle self-standing. In recent times, PET bottles have been made in one piece with a self-standing petaloid-shaped base [3].

The desirable properties of PET (clear, lightweight, high strength, stiffness, favorable creep characteristics, low flavor absorption, high chemical resistance, barrier properties and low price) make it the material of choice for carbonated soft drinks containers, fibers and films [1]. Due to low cost, better aesthetic appearance, and better handling, PET is being preferred over polycarbonate (PC) polymers [4].

PET has been also known for many years as a textile fiber forming material. But lately, it has started to be used in extrusion foam processing for textile fibers because of its elastic nature [5]. PET is also used as a recyclable polymer, and the markets for recycled PET (R-PET) are growing by the year.

3. Crystallization behavior of PET

'Crystalline' means that the polymer chains are parallel and closely packed, and 'amorphous' means that the polymer chains are disordered [8]. Most polymers exist as complex structures made up of crystalline and amorphous regions. Crystallinity is usually induced by heating above the glass transition temperature (T_g) and is often accompanied by molecular orientation [6]. It is impossible to reach 100% crystallinity with the lowest free energy because polymers do not have a uniform molecular weight.

Instead, the polymers can only react to produce partly crystalline structures, usually called "semicrystalline" [7].

The degree of polymer crystallinity depends on both intrinsic and extrinsic factors. Narrow molecular weight, linear polymer chain structure, and high molecular weight are very important pre-conditions in terms of obtaining high crystallinity [8]. Crystallinity is also affected by extrinsic factors, like stretch ratio, mode of extension and crystallization temperature in the preparation of polymer films [9]. Below the glass transition temperature, polymer chains are rigid; after reaching the glass transition temperature, the chains become more flexible and are able to unfold under stress. If the temperature is above T_g and stretching is carried out, the randomly coiled and entangled chains begin to disentangle, unfold, and straighten and some of them even slide over their nearest neighbor chains [10].

PET is a crystallizable polymer because of its regularity in chemical and geometric structures. It is either in the semi-crystalline state or in the amorphous state. The levels of crystallinity and morphology significantly affect the properties of the polymers [11]. Even with limitations in its barrier properties and mechanical strength, crystalline PET is still widely used. Polymers with high crystallinity have a higher glass transition temperature T_g (T_g is 67 °C for amorphous PET and 81 °C for crystalline PET) and have higher modulus, toughness, stiffness, tensile strength, hardness and more resistance to solvents, but less impact strength [11,12].

Crystallinity in PET is usually induced by thermal crystallization and/or by stress or strain induced crystallization. Thermally induced crystallization occurs when the polymer is heated above T_g and not quenched rapidly enough. In this condition the polymer turns opaque due to the spherulitic structure generated by thermal crystallization aggregates of un-oriented polymers [13]. In stress-induced crystallization, stretching or orientation is applied to heated polymer and the polymer chains are rearranged in a parallel fashion and become closely packed [14]. The crystallization process is composed of nucleation and spherulitic crystallization, and may occur at temperatures above T_g and below the melting point T_m [15]. Quenching the melt quickly results in a completely amorphous PET [12].

Crystalline polymers have a heterogeneous structure due to the interspersed amorphous regions while amorphous polymers in all their forms (melts, rubbers, glasses, etc.) have a homogeneous structure. Polymers are characterized by a glass transition temperature T_g and a melting temperature T_m [16]. The glass transition behavior of semi-crystalline polymers are greatly affected by the factors affecting degree of crystallinity such as molecular weight, amount of crystalline phase and morphology [11, 15, 17]. The glass transition temperature of semi-crystalline polymer is higher and broader than that of the amorphous polymer [11].

Crystalline polymers are characterized by a T_m and amorphous polymers are characterized by a T_g . At the melting point, polymers are like a rubber-liquid. For crystalline polymers, the relationship between T_g and T_m has been described as follows [8].

$$T_g \rightarrow \frac{2}{3}T_m \quad (\text{for unsymmetrical chains}) \quad (\text{Equation 1})$$

and

$$T_g \rightarrow \frac{1}{2}T_m \quad (\text{for symmetrical chains}) \quad (\text{Equation 2})$$

PET has a T_g between 340 to 353 K (67 to 80 °C) and a T_m of 540 K (267 °C). The crystallization of PET has been widely investigated. The Avrami equation was adopted by [18], with using the density balance method, where the amorphous fraction was calculated from the final density at that condition, rather than the density of 100% crystalline PET. X-ray analyses and polarizing microscopy were used to observe crystalline structures. Different structures could be obtained by adjusting crystallization temperature or previous melt conditions. The maximum rate of crystallization occurs at 180 °C. Further research in this subject has also been reported [19]. Studies have been conducted on the kinetics of crystallization of different commercial PET materials in terms of the Avrami equation with a Differential Scanning Calorimetry (DSC) method and confirmed that the rate constant k is very sensitive to crystallization temperature [20]. Different PET samples have different crystallization mechanisms. With increasing crystallization temperature, spherulite diameter increases [21]. Ozawa studied the kinetics of dynamic crystallization of PET. He obtained crystallization curves through DSC at different cooling rates [22]. A modified Avrami equation was applied to the primary crystallization in a non-isothermal situation. Jabarin compared the crystallization rate parameters of both isothermal and dynamic processes, and found that they are similar to each other in terms of mechanisms of crystallization. A method was developed to predict the minimum cooling rate required to obtain non-crystalline PET [23]. DSC spectrum of PET is shown in figure 1.

In addition to time and temperature, many other factors such as pressure, the degree of molecular orientation and environment have influence on crystallization mechanism, morphology, and final properties of PET [24, 25]. Nucleating agents also affect the crystallization of PET. Some studies have investigated the effect of the additives on crystallization behavior [11, 26].

Jiang et al have studied the effects of three kinds of nucleating agents, including talc, sodium benzoate and an ionomer (Ion., Na^+) on the crystallization kinetics of PET by using DSC. They have used Avrami and Ozawa equations to obtain the parameters of the isothermal and the nonisothermal crystallization kinetics, respectively. They concluded that three nucleating agents can increase the crystallization rate of PET, and sodium benzoate has the most excellent nucleating effect for the crystallization of PET with the same content of nucleating agent. The crystallization mode of PET might shift from three-dimensional growth to two dimensional growth by the addition of the nucleating agents [42].

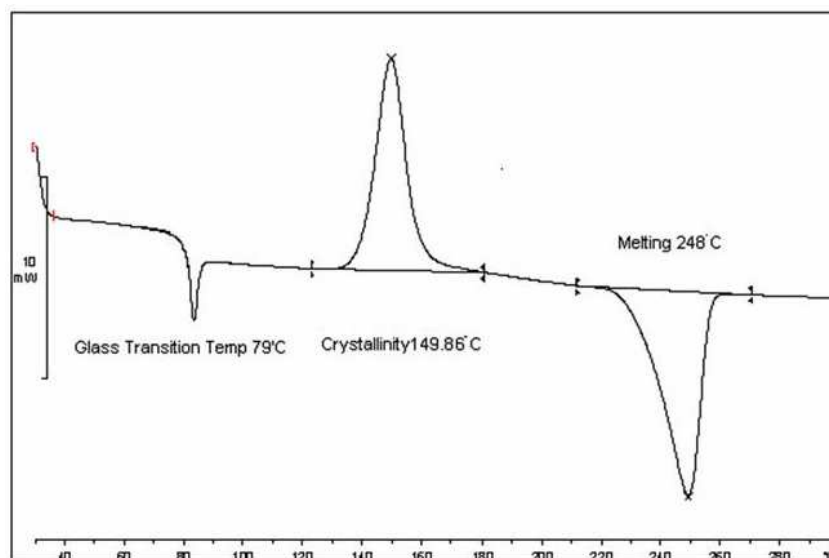


Figure 1. DSC spectrum of PET.

The crystallization behavior of PET with and without catalysts has been compared by [41]. They found that nucleation has a great influence on overall crystallization rate at low temperatures near T_g . Moisture and molecular weight have a great effect on crystallization [23, 27]. It is found that the kinetics of crystallization depends on molecular weight and that with increasing percentage of moisture, the half-time crystallization and induction time of crystallization decrease. Spherulite growth rate was independent of water absorbed [20].

In a study with characterization methods for PET, different experimental methods have been investigated by Faraj et al. They have used different techniques such as X-ray diffraction (XRD), energy dispersive X-ray (EDX), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), atomic force microscopy (AFM) and UV spectrophotometer for characterization of the structural, thermal and optical properties of PET. The surface morphology and optical transmittance of PET substrate have been reported. They recommend that high quality films on PET substrate give the possibility to use as alternative substrates to the conventional glasses [43]. XRD patterns of PET, EDX spectrum of the PET and AFM analysis of PET are shown in figure 2, figure 3 and figure 4 respectively.

Stress is an important factor, affecting crystallization. The effect of stress-induced crystallization of PET has been investigated with density measurements, wide-angle X-ray diffraction and small-angle light scattering measurements [28]. Amorphous PET films were stretched at constant strain rates below and above T_g . The stress-induced crystallization has also been analyzed as a function of time and orientation level [29].

Marco et al. focused on the crystallinity induced by stretching PET at temperatures above the glass transition and on the influence of stretch and blow molding parameters on the properties of the final product [30].

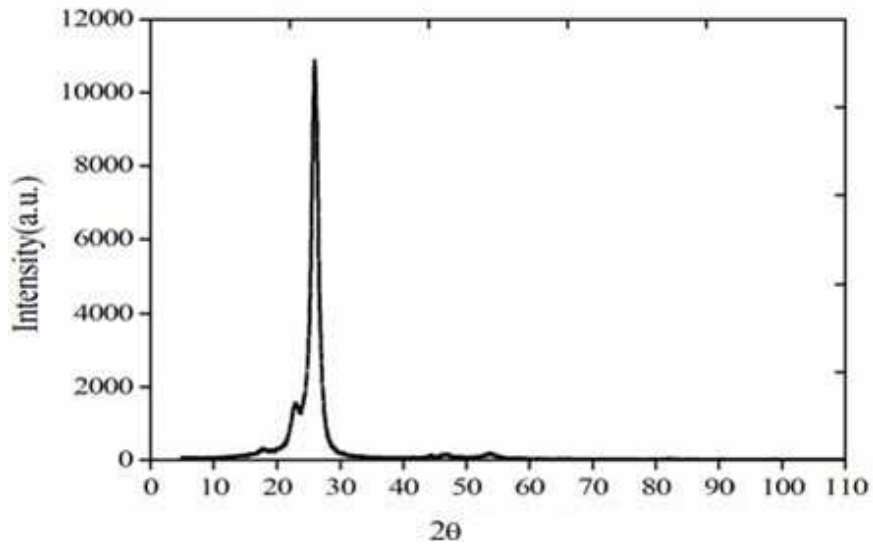


Figure 2. XRD patterns of PET.

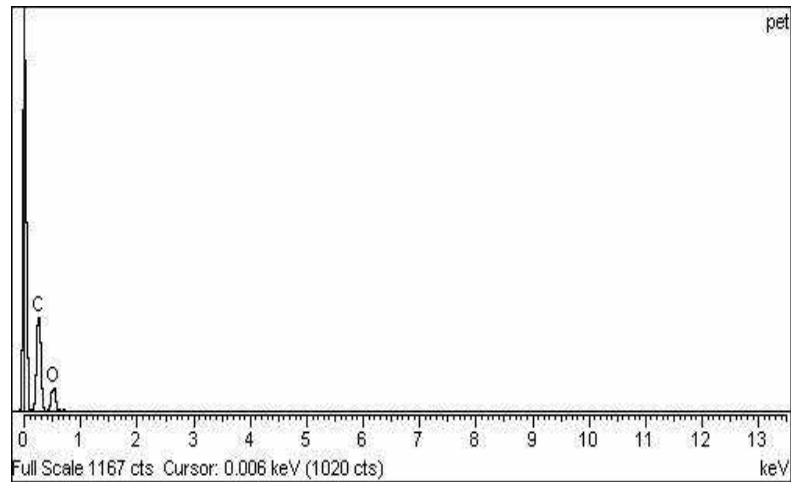


Figure 3. EDX spectrum of the PET.

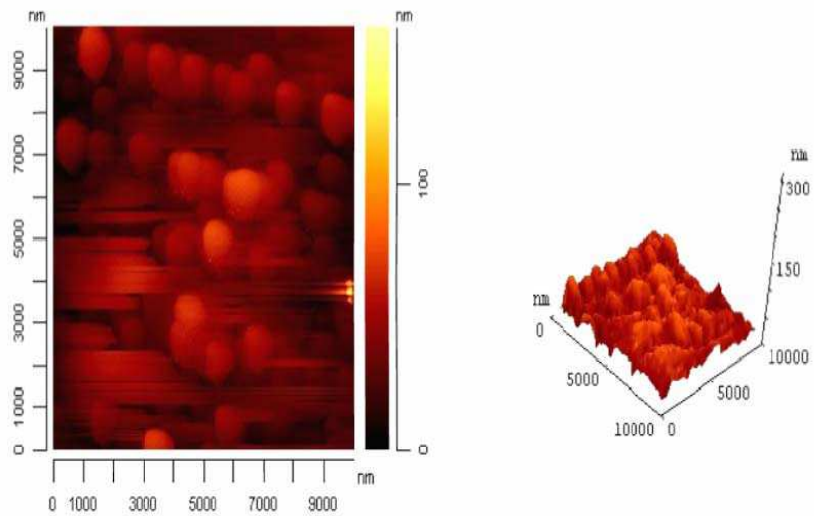


Figure 4. AFM analysis of PET.

A study has been conducted with PET material and found that reducing the shot size (amount of material injected into the mould cavity) will minimize crystallinity while hold time (length of time the gate remains open allowing more material to be pushed into the mold cavity) has no effect at the lower shot size. However, with a larger shot size, a low hold time is necessary to reduce crystallinity. The least crystallinity occurs with minimum hold time and minimum shot size [31].

In a study conducted by Hanley et al., it was found that the extent of the orientation and crystallinity depends upon the geometry of the bottle base, and that there is an abrupt change from the amorphous region to the crystalline regions. The valley and the transition region to the foot are the most biaxially oriented regions of the base. The orientation in the middle of the foot is more circular and the crystallization is less. This shows that the stretch in this region is more uniaxial (or less biaxial) but crystalline lamellae are still observed [32].

Some experimental works has been conducted on the orientation and crystallization of PET films subjected to uniaxial or biaxial drawing under industrial processing conditions [38-40]. The changes in the degree of orientation and crystallinity have been investigated using the wide-angle X-ray scattering (WAXS) technique [39]. By analyzing the crystalline diffraction patterns, they found that the orientation of the developing crystals depends on the relation of the draw rate and temperature to the chain relaxation process and that the crystallization rate is highly temperature dependent. Everall et al. used polarized attenuated reflection infrared spectroscopy to quantify biaxial orientation in PET films and stretch blow molded bottles [41].

Crystallization may be due to many nuclei centres forming small spherulites at low temperatures. Larger crystal structures may be obtained when the material is crystallized at higher temperatures or by slow cooling from the melt but 100% crystallinity is never possible in normal processing conditions [15, 17]. Usually the percentage crystallinity is lower than 90% [17]. In general, polymeric materials are semicrystalline with crystalline and amorphous phases co-existing [38]. Mixed amorphous crystalline macromolecular polymer structure is shown in figure 5 [38].

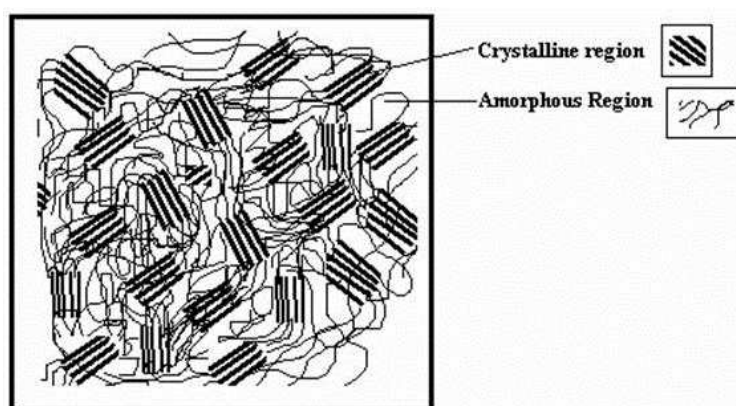


Figure 5. Mixed amorphous crystalline macromolecular polymer structure [38].

The morphology is described by the spherulite radius, lamellar thickness and long period; distance between two adjacent lamellae. Small angle light scattering microscopy and X-ray analyses are usually applied to obtain these parameters [15]. Even at the same crystallinity content, samples crystallized at higher temperature are more opaque and brittle [18]. Samples with smaller spherulite sizes have higher yield stress, lower ultimate elongation and high brittleness temperature and higher impact strength [40].

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